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13. ABSTRACT (Maximum 200 words)

Mass spectrometry, anion photoelectron spectroscopy and density functional theory calculations have been applied to several aluminum oxide cluster complexes. The reactivity of several "magic" clusters (i.e., those species that dominate the mass spectrum) toward water and methanol has been explored, and for one system, $Al_3O_3^-$ + 1 and 2 H_2O, the reaction products have been determined by comparing experimental and computational results. The Density functional theory calculations have been successfully applied to a number of transition metal complexes with the intent that they will be applied in the future to transition metal disulfide cluster systems. Preliminary results on the spectra of larger hypermetallic aluminum oxide clusters are presented.

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(Continuation Sheet)

Probing metal cluster and metal oxide cluster interactions with organo-sulfur and organo-phosphorus molecules using mass spectrometry and anion photoelectron spectroscopy

(1) List of Manuscripts

"Separating contributions from multiple structural isomers ion anion photoelectron spectra: $Al_3O_3^-$ beam hole burning," F. Ahu Akin and Caroline Chick Jarrold, J. Chem. Phys. **118**, 1773-8 (2003).

"Addition of water and methanol to $Al_3O_3^-$ studied by mass spectrometry and anion photoelectron spectroscopy," F. Ahu Akin and Caroline Chick Jarrold, J. Chem. Phys. **118**, 5841-51 (2003).

"A comparison of stable carbonyls formed in the gas-phase reaction between precious metal atomic anions and methanol: Anion photoelectron spectroscopy and density functional theory calculations on $HNiCO^-$, $PdCO^-$ and $PtCO^-$," Bappaditya Chatterjee, F. Ahu Akin, Caroline Chick Jarrold and Krishnan Raghavachari, J. Chem. Phys. **119**, 10591-9 (2003).

"Reactivity of $Al_3O_3^-$ cluster toward water studied by density functional theory," F. Ahu Akin and Caroline Chick Jarrold, accepted for publication, J. Chem. Phys., January, 2004.

"Comparison of nickel-group metal cyanides and acetylides and their anions using photoelectron spectroscopy and density functional theory calculations," Bappaditya Chatterjee, F. Ahu Akin, Caroline Chick Jarrold and Krishnan Raghavachari, submitted to J. Chem. Phys., October 2003.

(2) Scientific Personnel

Dr. F. Ahu Akin was the a graduate student dedicated to this project. She is presently a postdoctoral researcher at University of Nevada, Reno.

(3) Report of Inventions

none

(4) Scientific progress and acomplishments

Over the last year (the duration of the grant), studies initiated on several aluminum oxide species and their reaction with water an methanol have been brought to a conclusion, and studies extended to larger aluminum oxide species have been initiated. Further, the structures of complexes formed in the high-pressure reactions between transition metals and small organic molecules have been determined both spectroscopically and by density functional theory calculations. Note that this work is by and large a continuation of the ARO YIP grant transferred from the University of Illinois, Chicago (August, 1999 to June, 2002). Relevant background information can be found in the final report submitted through that University.

DFT Calculations on $Al_3O_4H_2^-/Al_3O_4H_2$ and $Al_3O_5H_4^-/Al_3O_5H_4$- Previously, we found that when the "magic" number cluster, $Al_3O_3^-$ is exposed to water or methanol in the gas phase, new "magic" masses appear in the mass spectrum corresponding to the addition of one or two solvent molecules to $Al_3O_3^-$. $Al_3O_3^-$ had previously been the subject of several theory papers, and was found to have two energetically-competitive structural isomers having kite-like and distorted rectangular structures. The two structures have different Lewis-acidities on their constituent aluminum atoms, and therefore presented an interesting case for studying structure-based reactivity. Based on our mass spectrometric and anion photoelectron spectroscopic results [J. Chem. Phys. **118**, 5841-51 (2003)], we proposed that water and methanol molecules were dissociatively adsorbing onto $Al_3O_3^-$, and that the system became chemically saturated with two additions.

We further proposed that the thermodynamically stable $Al_3O_5H_4^-$ structure was a rectangle-based structure in which hydroxides added to the central aluminum atom, and that the dissociated –H's added to the equivalent corner O-atoms. To determine the viability of our hypothesis, we performed an extensive set of DFT calculations on a wide range of reaction complex structures, both anions and neutrals, based on the both the kite and rectangular structures separated out in our ion beam hole-burning experiments [J. Chem. Phys. **118**, 1773-8 (2003)], and based both in H-bonding (charge-dipole interactions), Lewis acid/base interactions, and dissociative adsorption. DFT calculations at the B3LYP/aug-cc-pVTZ level were done using the Gaussian software package [M. J. Frisch *et al.*, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998].

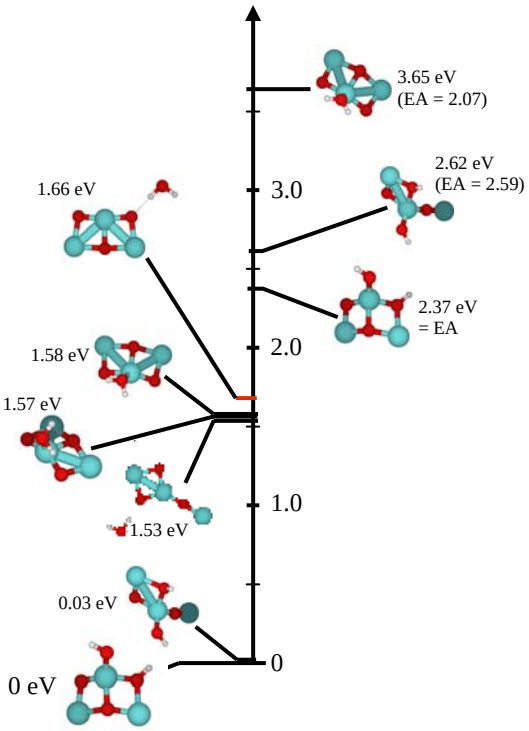

Figure 1. Structures of $Al_3O_4H_2^-$ and neutrals determined from DFT calculations (B3LYP/aug-cc-pVTZ)

Figures 1 and 2 show a summary of the results of the calculations on the singly-hydrated and doubly-hydrated complexes, respectively. Structures have their optimized energy pointed out on the energy scale, which is zeroed on the lowest energy structure (the global minimum). Electron affinities (EA) are determined by the energy difference between like structures, since transitions between anions and neutrals with disparate structures will not be observed because of zero Franck-Condon overlap and one-electron propensity rules. Several of the complex structures in both Figs. 1 and 2 have kite and rectangle moieties that are left fairly unperturbed. For both figures, the anion structures are on the left side of the energy axis, and the neutral structures are found on the right. Note that in both cases, complexes that have undergone dissociative attachment of water are energetically favored over more weakly bound systems, while Lewis acid/base-type structures and charge-dipole dominated structures are energetically comparable. It should be pointed out that the figures do not show structures having initial guesses that did not converge in the calculations, which were numerous.

The interesting feature in Fig. 1 is that there are again two energetically competitive structures for both the anion and neutral, and they can still be described as being kite structure- and rectangle structure-based. They both involve dissociative attachment of water, and because of the energetic proximity of the two anions and the two neutrals, they have very similar electron affinities. One of the baffling issues surrounding the interpretation of the PES of the hydrated $Al_3O_3^-$ clusters wass that the spectrum of the singly hydrated complex was much more congested than that of the doubly hydrated complex [J. Chem. Phys. **118**, 5841-51 (2003)]. The calculations on the singly hydrated complexes explain the congested appearance of the $Al_3O_4H_2^-$ PE spectra: Two anion structures of $Al_3O_4H_2^-$ populate the anion beam generated in our laser ablation/pulsed molecular beam source, and they have fairly close detachment energies.

Figure 3 shows the experimentally-obtained PE spectrum of $Al_3O_4H_2^-$ (dotted trace) with two spectral simulations superimposed. The simulation denoted N1-A1 is based on the structures, normal coordinates and vibrational frequencies of the ground state anion to ground state neutral transition. These are the rectangle-based hydroxide anion and neutral states. The N2-A2 simulation is based on the structures, normal coordinates and vibrational frequencies of the low-lying excited kite-based anion and neutrals. Note that the calculations predict them to overlap, though we do not take the calculated energy spacing to be accurate enough to definitively assign the broad masses of signal in the spectrum. What we can take away from this figure, though, is that the calculations predict congestion based on the presence of two isomers in the anion beam, both with similar detachment energies, and both expected to have broad transitions to their respective neutral ground states.

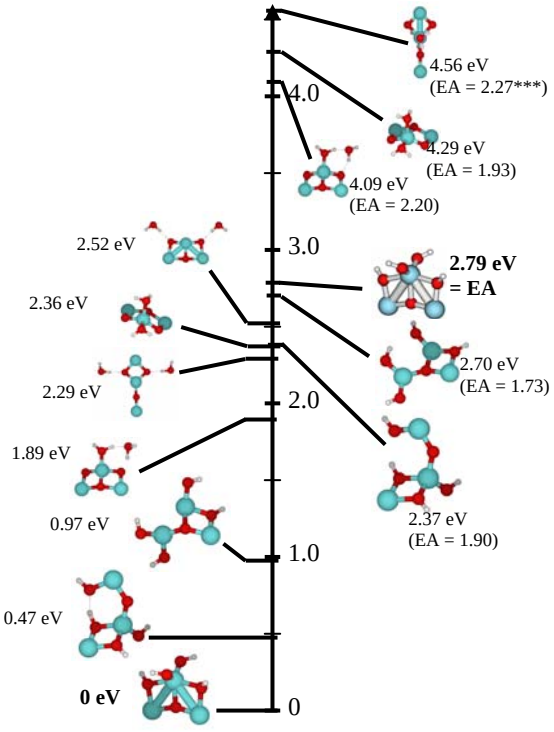

Figure 2. Structures of $Al_3O_5H_4^-$ and neutrals determined from DFT calculations (B3LYP/aug-cc-pVTZ)

Referring back to Fig. 2, another interesting feature emerges. The kite-based and rectangle-based dihydrates, which represent the first excited and ground state structures, respectively, have separated energetically enough that we believe that the ion beam is populated only with the ground state rectangle structure. However, when calculating the electron affinity predicted for this species based on the optimized neutral structures, we see that the neutral rectangle based structure that closely resembles the ground anion state is actually the second excited neutral state. The predicted rectangle-based electron affinity is 2.79 eV, which is substantially higher than the electron affinities predicted for the other structures.

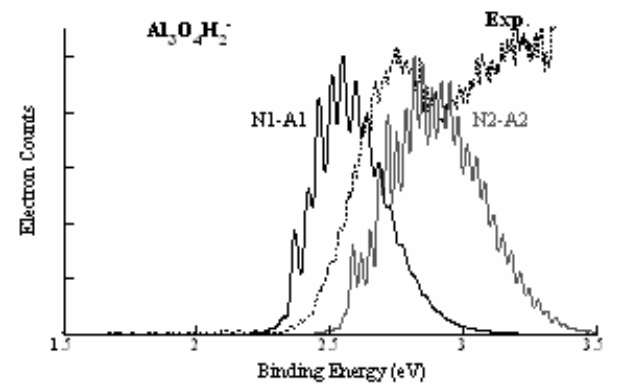

Figure 3. Anion PE spectrum of $Al_3O_4H_2^-$ (dotted trace) along with simulations based on the ground state anion to neutral transition (rectangle hydroxide, N1-A1) and the low-lying excited state transition (kite hydroxide, N2-A2)

The PE spectrum of $Al_3O_5H_4^-$ and $Al_3O_5D_4^-$ (the latter included because is shows partially-resolved vibrational steps in the ground state band) with the simulation based on the rectangle-based anion and neutral structures, normal coordinates, and vibrational frequencies. Note that the onset of signal in the experimental spectrum, which is approximately 3.14(5) eV, is higher than any of the electron affinities for the various structures predicted in the calculations, but is in reasonable agreement with the electron affinity predicted for the rectangle-based dehydrate (2.79 eV). We did not perform any excited state calculations for the neutral structure, which is why only one simulated band is shown. Again, the simulation from the calculated parameters cannot be used to definitively assign the spectrum, but it is the most consistent with the observed spectra.

<u>DFT Calculations on transition metal atom-containing complexes</u>- We wish to extend our metal oxide reactivity studies from Al_xO_y clusters to transition metal oxides and sulfides, which will again rely heavily on the interplay between theory and experiments. Therefore, in collaboration with Prof. Krishnan Raghavachari, we did a series of DFT calculations on a series of Ni, Pd and Pt unsaturated complexes. We had previously obtained the PE spectra of complexes formed in the reactions between these atoms and methanol, ethylene, and acetonitrile in the gas phase, and had found a general theme of dehydrogenization by the metal atoms coupled with the addition of a single ligand for Pd and Pt, while Ni tended to be doubly ligated. In general, the calculations gave very accurate electron affinities and ground state structures and vibrational frequencies, while excitation energies for the multitude of excited states found in unsaturated transition metal complexes were not as accurate. We also determined that the calculations tended to underestimate the electron affinities of the nickel complexes (agreement was very good for the Pd and Pt complexes). The spectra were all simulated using calculated structures, normal coordinates and vibrational frequencies, as in the case of the $Al_3O_3 + H_2O$ complexes. Since the spectra and simulations are numerous (NiCN, HNiCO, $HNiC_2H$, $Ni(C_2H)_2$, PdCO, PdCN, PdC_2H, PtCO, PtCN, PtC_2H), they are not included in this report, but can be found in the papers cited above.

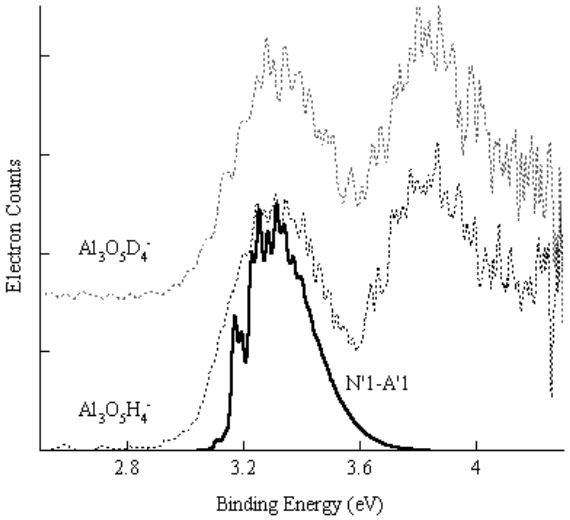

Figure 4. PE spectra of $Al_3O_5H_4^-$ and the deuterated analog, along with a simulation of the $Al_3O_5H_4^-$ spectrum based on the parameters determined from DFT calculations on the ground anion state and its neutral analog

<u>PE Spectra of larger $Al_xO_y^-$ clusters</u>- The $Al_3O_3^-$ studies showed how the atomic arrangement in a cluster could impact on its reactivity toward, for example, and electron donating solvent. We believe we can take the reactivity of $Al_3O_3^-$ and extend it to larger clusters observed in the mass spectra of our $Al_xO_y^-$ cluster source. We have already observed interesting trends in the mass spectra. For example, $Al_xO_y^-$ clusters with x = odd tend to by hypermetallic (x/y greater than 2/3, the bulk stoichiometric ratio) while those with x = even tend to be hyperoxide (x/y less than 2/3). The electron affinities of the hyperoxide clusters are much larger than the electron affinities of the hypermetallic clusters, and in fact, given the photon energies available to us (until just recently) we have been unable to measure the PE spectra of the hyperoxide clusters. The hypermetallic clusters, however, are potentially more interesting from the standpoint of designing a catalytic material that is more immune from catalytic poisoning.

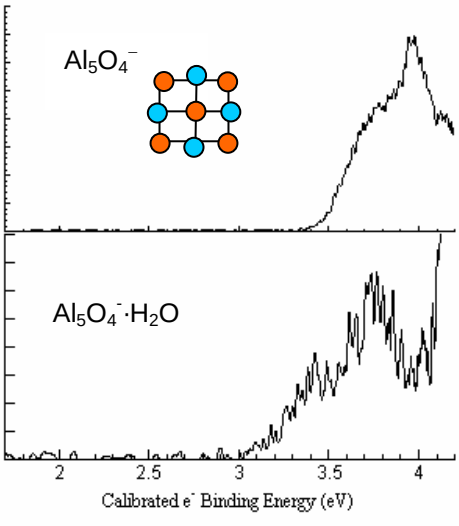

Figure 5. PE spectra of $Al_5O_4^-$ and $Al_5O_4\cdot H_2O$

As an example of this, $Al_5O_4^-$ is the next "magic" cluster in the anion mass spectrum of $Al_xO_y^-$ clusters. The PE spectrum of $Al_5O_4^-$ is shown in the top panel of Figure 5. Note that, the electron affinity is relatively high compared to the two structures of $Al_3O_3^-$. In fact, preliminary calculations suggest that the structure is a puckered square, and that for this particular species, there are no other close-lying structural isomers. We have been able to get very preliminary spectra of the complex formed with the addition of one water molecule to $Al_5O_4^-$, and this is shown in the lower panel of Fig.5. Aside from the signal to noise disparity, it is fairly similar to the $Al_5O_4^-$ spectrum, except that the rising edges are shifted to lower binding energy. This suggests that one of two things may be happening: First, the water may be physisorbing to the cluster by way of Lewis acid/base interactions with the central Al atom, and the complex photodissociates with the first 4.66 eV photon, leaving free water and vibrationally excited $Al_5O_4^-$. This vibrationally hot anion can then absorb a second photon, yielding a vibrationally hot PE spectrum (which would appear shifted to lower binding energy, as we observe). Second, the water may again be physisorbing to the cluster via Lewis acid/base interactions, and it remains bound upon photodetachment, but the anion is slightly destabilized by the excess charge from the electron donation by H_2O into the LUMO of $Al_5O_4^-$. This, too, would result in the shift of the spectrum to lower binding energy. This is again a situation in which calculations will be invaluable for interpreting the spectra more definitively. However, at this point it is useful to point out that the water appears to be attaching intact, unable to dissociate because there is no place for the –H to attach, given that all of the oxygens are already bound to three aluminum atoms. This early results suggests that more resilient catalysts may be found in hypermetallic materials.

We have also obtained preliminary spectra of the $Al_7O_y^-$ series for y = 5 – 8. These are shown in Figure 6. These systems are interesting because they show a discontinuity in the trend in electron affinity between y = 6 and y = 7. That is, as a metal oxide cluster becomes more oxidized, the electron affinity is expected increase until peroxide species form, at which point the electron affinity drops down. The discontinuity may be due to an onset of energetically competitive structural isomers at y = 7. These spectra are present undergoing more signal averaging, and will be the subjects of subsequent reactivity studies.

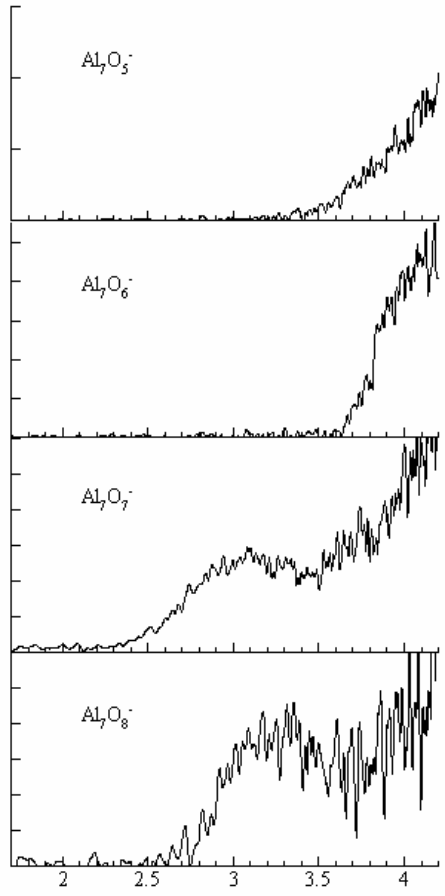

Figure 6. PE spectra of $Al_7O_y^-$ clusters.

(5) Technology transfer

none

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